

Characterization of triadimefon sorption in soils using supercritical fluid (SFE) and accelerated solvent (ASE) extraction techniques

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Abstract: Sorption–desorption of the fungicide triadimefon in field-moist silt loam and sandy loam soils were determined using low-density supercritical fluid extraction (SFE). The selectivity of SFE enables extraction of triadimefon from the soil water phase only, thus allowing calculation of sorption coefficients (K_d) at field-moist or unsaturated conditions. Triadimefon sorption was influenced by factors such as soil moisture content and temperature; sorption increased with increased moisture content up to saturation, and decreased with increased temperature. For instance, K_d values for triadimefon on the silt loam and the sandy loam soils at 40 °C and 10% water content were 1.9 and 2.5 ml g⁻¹, respectively, and at 18% water content, 3.3 and 6.4 ml g⁻¹, respectively. Isosteric heats of sorption (ΔH_i) were -42 and -7 kJ mol⁻¹ for the silt loam and sandy loam soils, respectively. Sorption–desorption was also determined using an automated accelerated solvent extraction system (ASE), in which triadimefon was extracted from silt loam soil by 0.01 M CaCl₂. Using the ASE system, which is basically a fast alternative to the batch equilibration system, gave a similar ΔH_i value (-29 kJ mol⁻¹) for the silt loam soil ($K_f = 27 \mu\text{g}^{1-1/n} \text{ml}^{1/n} \text{g}^{-1}$). In order to predict transport of pesticides through the soil profile more accurately on the basis of these data, information is needed on sorption as a function of soil water content.

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1 INTRODUCTION

Sorption is one of the main processes determining the fate of organic pollutants, such as pesticides, in the soil. Thus, correctly determined sorption coefficients (K_d) are of great importance for an understanding and prediction of pollutant behavior in the environment. Traditionally, techniques for determination of K_d values, such as batch slurry methods, are performed at unrealistic ratios between soil and water not found in the field, ie a small amount of soil is equilibrated with a large amount of water. Furthermore, batch slurry methods involve shaking and centrifugation, mechanical treatments that may change the physical and chemical characteristic, which in turn may affect sorption behavior of the soil.

Thus, development of a technique whereby sorption can be characterized in field-moist or unsaturated soils is of great importance. A technique that is promising in this respect is the use of supercritical fluid extraction

(SFE). SFE has primarily been used for quantitative extraction of organic compounds, such as pesticides, from a variety of environmental matrices.^{1,2} Rochette and Koskinen^{3–5} recently developed a technique that uses the selectivity of SFE to extract atrazine from the soil solution surrounding the soil particle without also extracting residues bound to the soil particles. This allowed characterization of sorption–desorption in field-moist or unsaturated soil.

The SFE-sorption technique thus far has only been used for determination of sorption of atrazine^{3–5} and linuron⁶ in unsaturated soils. Further validation of the method is needed for other classes of pesticide, since the technique may not be applicable to all pesticides. It appears that sorption–desorption of some very polar pesticides (ie imidacloprid, unpublished data) cannot be characterized using this technique. Therefore, triadimefon, an azole fungicide of medium polarity (log $P = 3.1$, water solubility 64 mg litre⁻¹),⁷

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was used in this study. Triadimefon is reported to be moderately sorbed in soils, with both clay and organic carbon content being important for the sorption behavior.^{8,9} The effects of soil properties, moisture content and temperature on sorption–desorption in field-moist soils were evaluated. Sorption–desorption was also characterized using an automated modified batch slurry technique developed in our laboratory, whereby an accelerated solvent extraction (ASE) system¹⁰ was used to sequentially desorb (extract) triadimefon from soil with 0.01 M calcium chloride solution.

2 EXPERIMENTAL PROCEDURES

2.1 Chemicals/soils

Pure analytical triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone, (>99% purity) was purchased from Chem Service (West Chester, PA, USA), and [*ring*-U-¹⁴C]triadimefon (radiochemical purity, > 97.6%; specific activity, 25.3 mCi mmol⁻¹) was obtained from Bayer Corporation (Stilwell, KS, USA). SFC/SFE grade carbon dioxide was obtained from Air Products and Chemicals Inc (Allentown, PA, USA). Pesticide grade methanol and calcium chloride were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Ecolite scintillation cocktail (ICN, Costa Mesa, CA, USA) was combined with SF-CO₂ extracts for ¹⁴C quantification by liquid scintillation counting. A sandy loam soil (Mellby, Sweden, Fluventic haplumbrept) and a silt loam soil (Waukegan, US, Typic Hapludoll) were used in this study. Some physical and chemical characteristics of the soils are listed in Table 1.

2.2 Sample preparation

2.2.1 Supercritical fluid extraction

Subsamples of field-moist soil (5.0 g) were treated with 1 ml of a methanol solution containing analytical and ¹⁴C-labelled triadimefon giving final concentrations of 10 µg g⁻¹ (*K_d* experiments) and 1, 5 and 10 µg g⁻¹ (*K_f* experiments). The radioactivity in the samples varied between 0.2 and 1.6 kBq g⁻¹ soil, depending on triadimefon concentration and technique used. Original soil moisture contents were determined after oven drying at 105 °C for 24 h. The soils were mixed with the spike solution and approximately 0.5 ml water, and air-dried back to their original weights at room temperature to ensure removal of methanol from the soil. To obtain greater water contents, deionized water was added to the spiked soil in the weighing boats and mixed thoroughly. The soil was weighed into the

extraction thimbles and equilibrated for 24 h before extraction.

2.2.2 Accelerated solvent extraction

Subsamples of field-moist soil (10.0 g) were spiked at three different concentrations (5, 10 and 20 µg g⁻¹) using the procedure described in Section 2.2.1. The soil was transferred to the ASE cell, sandwiching the soil between plugs of Hydromatrix (Varian, Harbor City, CA, USA) to avoid dead volumes, and equilibrated for 24 h before extraction.

2.3 Sorption–desorption: field moist soils

Supercritical fluid-CO₂ sorption experiments were performed in triplicate using a HP 7680A supercritical fluid extractor (Hewlett Packard, Little Falls, DE, USA). The extractor, which was equipped for 7-ml extraction thimbles, had a variable-diaphragm nozzle preceding the cryotrapping system. Octadecylsilane-bonded (C18, 5 µm) silica was used as trapping material. The soil in the extraction thimble was extracted with supercritical carbon dioxide (SF-CO₂) at 0.25 g ml⁻¹.

Ten 5-min sequential extraction periods were used for each sample. Between sequential extraction periods, 7 min elapsed (desorption equilibrations) during depressurization, rinsing of the cryotrap, and weighing of the sample vessel to determine water losses. Extractions were performed at 40, 50 and 60 °C. Trap and nozzle temperatures were 10 and 55 °C, respectively, except for the extraction at 60 °C, when the nozzle temperature was 65 °C. The trap was warmed to 35 °C and the nozzle temperature was lowered to 45 °C during the trap rinse substep. The trap was rinsed twice after extraction with 1.4 ml of methanol into two empty vials.

The SFE extract was combined with scintillation cocktail and the radioactivity in the solution, *R_w* (Bq), counted with a Packard 1500 Tri-carb Liquid Scintillation Analyzer (LSC) (Downers Grove, IL, USA). The radioactivity on soils, *R_s* (Bq) was calculated from the difference *R_i* (total initial radioactivity) minus *R_w*. Mass balances of ¹⁴C were determined by combusting triplicate subsamples of the extracted soil using a Packard 306 sample oxidizer and quantifying the released ¹⁴CO₂ by LSC. Average mass balances of triadimefon for soils before and after SF-CO₂ extraction were 96 (±3)%, indicating that essentially all of the triadimefon applied to the soil was recovered from the trap or was still sorbed to the soil.

Sorption coefficients, *K_d* = ([*C_s*]/[*C_w*]), were calculated by measuring the distribution of triadimefon between soil ([*C_s*]), and soil water phase ([*C_w*]). The

Soil	Texture	Organic carbon (%)	Clay (%)	Silt (%)	pH ^a
Waukegan	Silt loam	1.8	22	46.2	5.5
Mellby	Sandy loam	3.4	10.4	10.2	6.2

^a Determined in 1 M KCl.

Table 1. Physical and chemical properties of soils used in this study

values of $[C_s]$ and $[C_w]$ were calculated from R_s and R_w , respectively, using the specific activity of the triadimefon and the mass of soil and the soil solution. Sorption coefficients for K_d -SE (sorption equilibration) and K_d -(D1 to D9) (nine desorption equilibrations) were calculated. Water contents at each equilibration were used in the calculations. The Freundlich equation,

$$x/m = K_f C^{1/n},$$

rewritten as

$$\log x/m = \log K_f + 1/n \log C$$

was used for calculation of the Freundlich sorption coefficient, K_f where x/m was the concentration of triadimefon on the soil after SFE ($\mu\text{g g}^{-1}$), C the concentration of triadimefon in the soil solution after SFE ($\mu\text{g ml}^{-1}$), and $1/n$ the slope of the sorption isotherm.

2.4 Sorption-desorption: modified automated batch method (ASE)

The ASE sorption experiments were performed in triplicate using a Dionex ASE 200 Accelerated Solvent Extractor (Sunnyvale, CA, USA), equipped with 33-ml cells. Soil samples were extracted for 15 min static extraction time with 0.01 M CaCl_2 at a pressure of 500 psi and temperatures of 25, 50 and 100 °C. The cell was rinsed with 60% of the extraction cell volume, and extracts were collected in 60-ml vials. The ASE extract was combined with scintillation cocktail and the radioactivity in the solution was measured as described for the SFE samples (Section 2.3).

The Freundlich equation, described above, was used for the calculation of K_p where x/m was the concentration of triadimefon on the soil after ASE ($\mu\text{g g}^{-1}$), C the concentration of triadimefon in the soil solution after ASE ($\mu\text{g ml}^{-1}$), and $1/n$ the slope of the sorption isotherm.

3 RESULTS AND DISCUSSION

The SFE technique developed to measure pesticide sorption in unsaturated soils is based on the assumption that the analyte is extracted from the soil water phase only, and not from the soil. The solubility power of a supercritical fluid is directly related to its density (ie temperature and pressure),¹¹ so that the solvent strength of SF-CO_2 increases with density. Therefore, mild extraction conditions with a low SF-CO_2 density (0.25 g ml^{-1}) and short dynamic extraction times were used to extract triadimefon from the soil solution while avoiding extraction of triadimefon sorbed to the soil. It was assumed that all the triadimefon was extracted from the soil water phase of the Waukegan and Mellby soils. In preliminary studies, extractions of a third soil, a loamy sand (0.5% OC), yielded much higher concentrations of triadimefon in SF-CO_2 at 0.25 g ml^{-1} density than during extraction of the Waukegan

or Mellby soil, indicating that the SF-CO_2 was not saturated with triadimefon during the extraction.

It seems unlikely that the mild SFE conditions, ie SF-CO_2 density = 0.25 g ml^{-1} , used in this study, would extract any triadimefon sorbed to the soil, since much harsher conditions were necessary for quantitative extraction. A preliminary study on the extraction of triadimefon from Waukegan soil showed that SF extraction efficiency was highly density-dependent, and quantitative extraction (95% recovery) could only be performed using harsh conditions (0.90 g ml^{-1} density, 20 min extraction). Unfortunately, there is no suitable method to measure extraction of very small amounts of triadimefon from the soil

3.1 Effect of soil properties: supercritical fluid extraction

The 24-h period after spiking of the samples is considered the sorption equilibration. The 7-min periods between the sequential sweep periods are the desorption equilibration periods (D1 to D9). Triadimefon sorption (SE) and desorption (D1 to D9) profiles obtained for the Mellby sandy loam and the Waukegan silt loam soils at 10, 15 and 18% soil moisture contents and at 40 °C are shown in Fig 1. The K_f (D1) and K_d values (SE and D1 to D9) were significantly higher for the Mellby than for the Waukegan soil at each water content. Since isotherm $1/n$ values were not the same for each soil at the different water contents, K_f values cannot be compared. Since K_d values were relatively constant through all desorption equilibrations (D1 to D9), except for the Mellby soil at 18% water content, which indicates that the soil/soil water equilibrium was reached after each desorption step, K_d -D1 values were selected for the comparisons of the effects of soil properties, water content and temperature on triadimefon sorption in unsaturated soil.

Values of K_d -D1 for Mellby and Waukegan soils at 15% water content and at 40 °C were 4.1 and 2.2 ml g^{-1} , respectively. Sorption of many pesticides to soil has been correlated with the nature and content

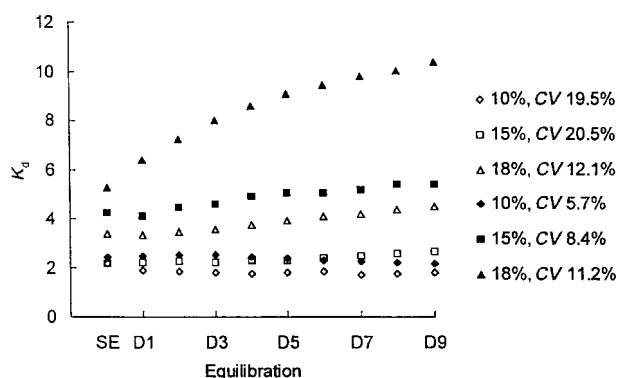


Figure 1. Sorption coefficient (K_d) values resulting from sorption equilibrations (SE) and desorption equilibrations (D1 to D9) for Mellby (solid symbols) and Waukegan (open symbols) soils at 40 °C and at different soil moisture contents (CV = coefficient of variation).

Table 2. SFE K_d and K_f values for Mellby and Waukegan soils at different water contents

Water (%)	Mellby				Waukegan			
	K_d	K_f	$1/n$	R^2	K_d	K_f	$1/n$	R^2
10	2.5	3.3	0.85	0.995	1.9	2.7	0.82	0.991
15	4.1	4.9	0.91	0.987	2.2	3.3	0.74	0.992
18	6.4	7.3	0.90	0.989	3.3	3.9	0.85	1.000

of the organic matter (%OC) and the soil clay fraction.¹² For these two soils, the Mellby had a greater K_d value than the Waukegan, which corresponds to a greater %OC for the Mellby soil (Table 1). Because K_{oc} -D1 values were the same for both soils (K_{oc} -D1 = (K_d -D1/%OC) \times 100) = 120), it appears that %OC was the main soil property affecting sorption. However, both %OC and clay content may have an important role in triadimefon sorption, especially in soils with high clay contents.⁸

3.2 Effect of water content

Changes in water content, when soils were below field capacity, significantly affected sorption for both soils (Fig 1, Table 2). For instance, K_d -D1 values for Mellby and Waukegan soils increased from 2.5 to 6.4, and from 1.9 to 3.3, respectively, when water content increased from 10 to 18%. Relatively linear relationships between K_d -D1 values and water contents were obtained for the Mellby ($R^2=0.95$) and Waukegan ($R^2=0.81$) soils. Similar results have been obtained with atrazine³ and linuron.⁶

The reason for the increase in sorption with increased water content, when below field capacity, is not entirely understood. It appears that, in these two soils, water content rather than potential affected sorption. As mentioned earlier, the K_{oc} -D1 values for both soils were 120 ml g⁻¹ at 15% soil moisture, which would be different water potentials. Similarly, K_{oc} -D1 values for the Mellby and Waukegan soils were 190 and 185 ml g⁻¹, respectively, at 18% soil moisture, which again would be different water potentials. The sorption-desorption equilibrium only depends on how much water there is in the system rather than how tightly it is held.

One explanation may be that a greater water content fills the void volume (pores) of the soil particles more effectively. Thus, water acts as a physical barrier causing inefficient SF-CO₂ extraction of triadimefon from water in some soil pores. The influence of water content on SFE performed using harsher conditions (higher densities) has previously been studied and both greater and lower recoveries with increasing water contents have been reported.^{13,14} Celis *et al*⁸ reported decreased triadimefon sorption at greater water-to-soil ratios in the batch equilibrium method, probably due to a lower number of available sorption sites in the soil/water mixture.

Results obtained in this and other studies³ show that even small changes in soil water content below field

capacity can greatly influence pesticide sorption, and thus the mobility of pesticides in soil. For instance, it would appear that the amount of pesticide immediately available for leaching through the soil depends on the water content just before the leaching event. Therefore, the influence of water on the sorption behavior is one of the main factors that should be incorporated into pesticide transport models.

3.3 Temperature effects

Supercritical fluid extraction sorption experiments were performed at three temperatures, 40, 50 and 60°C and at a constant water content of 15%. Measured K_d values for triadimefon decreased with increased temperature. Desorption coefficient K_d -D1 values were used for thermodynamic calculations. K_d -D1 values for Waukegan and Mellby soils at 40°C were 2.2 and 4.1, respectively, at 50°C, 1.5 and 3.7, and at 60°C, 0.8 and 3.5 ml g⁻¹. The decrease in sorption as a result of increased temperature probably resulted from an increase in solubility¹⁵ and volatility, and/or an easier desorption of the analyte molecules from the active sites of the matrix.¹⁶

Another approach to estimating binding strength of pesticides in soil is calculation of isosteric heats of sorption.¹⁷ Soil solution concentrations (ln C) at D1, at constant triadimefon sorption, were linearly related to the inverse of the temperature (T , K) (Fig 2). The slope of the regression line was used for calculating the isosteric heat of sorption ($\Delta H_i = R[\delta \ln C / \delta (1/T)]$). ΔH_i values were -42 and -6.9 kJ mol⁻¹ for Waukegan and Mellby soils, respectively. This further indicates that both %OC and clay fraction determine the triadimefon sorption behavior. Using ln C vs $1/T$ plots, K_d values for Waukegan and Mellby soils extrapolated to room temperature (21°C), were 6.5 and 4.8 ml g⁻¹, respectively. K_{oc} values (K_{oc} -D1 = (K_d -D1/%OC) \times 100) (21°C) for Waukegan and Mellby soils were 360, and 140, respectively, comparable to triadimefon batch values reported in the literature.^{8,9}

In order to compare ΔH_i values obtained with the SFE technique to those which would be obtained by a

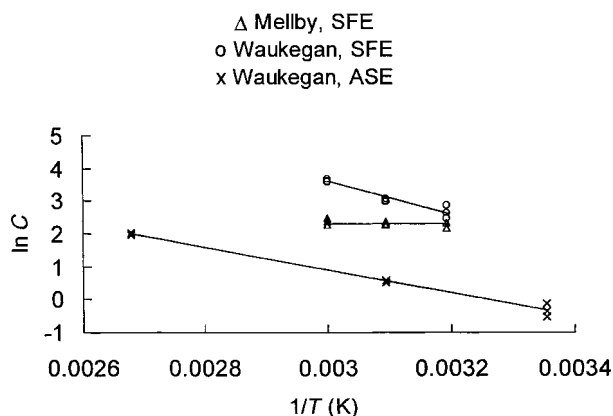


Figure 2. Variation of concentration of triadimefon in soil water (C) with temperature (T) for the Mellby and Waukegan soils. The slope is used for calculation of heat of sorption for D1 (SFE) and for SE (ASE).

batch technique, additional sorption experiments on the Waukegan soil were performed using the ASE instrument at three temperatures, 25, 50 and 100 °C. The ASE technique is commonly used as an alternative to Soxhlet extraction; the same solvents that are used in the Soxhlet are pumped into an extraction cell containing the sample, and rapid extraction is then performed at elevated temperature and pressure.¹⁰ The ASE application presented here used conditions comparable to batch equilibrium systems (0.01 M CaCl₂ at 25 °C) in order to desorb (extract) triadimefon from soil and determine sorption coefficients. Using the ASE technique, triadimefon sorption decreased with increased temperature. K_d values were 43, 17 and 4.2 ml g⁻¹ at 25, 50 and 100 °C, respectively. The isosteric heat of sorption, calculated as described above, was -29 kJ mol⁻¹ for the Waukegan soil, a result comparable to -42 kJ mol⁻¹ obtained with the SFE system (Fig 2). The discrepancy between the SFE and ASE plots and the concentration of triadimefon in the soil water can be explained by the different volumes of water used in the SFE (<1 ml) and in the ASE (~40 ml). K_f for the Waukegan soil at 25 °C was 27 µg^{1-1/n} ml^{1/n} g⁻¹ (1/n = 0.67). In comparison, batch sorption data of 14.6 µg^{1-1/n} ml^{1/n} g⁻¹ (1/n = 0.71) was obtained in a previous study on the Waukegan soil.⁸

4 CONCLUSIONS

The SFE technique described provides an opportunity to study the influence of different realistic soil moisture levels on pesticide sorption behavior, studies that are impossible to perform with conventional batch techniques. The SFE technique has been evaluated on a limited number of classes of pesticide, so that it is necessary to broaden the scope by including soils from other climatic regimes and other pesticides and organic pollutants. Among parameters of interest are interactions between analyte concentration and characteristics, water content and water potential, soil clay and organic carbon contents, and pH. It should be remembered that comparison of sorption values between the SFE and batch systems are difficult to make because the systems are so different and based on different assumptions.

The developed automated extraction system using ASE is a fast alternative to conventional batch techniques for determination of sorption. ASE also allows studies on the influence of temperature on sorption and the calculation of heats of sorption. Furthermore, the influence of analyte aging and moisture content on the sorption behavior can easily be studied by using spiked soils with different moisture contents: the samples are allowed to age, then extracted (desorbed) with 0.01 M CaCl₂ to determine the soil solution concentration, and the sorbed concentration determined with organic solvent. The ASE technique also

avoids potential artefacts due to shaking and centrifugation, which are inherent in the traditional batch slurry techniques.

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